

Impact of Top-ZrO₂ Nucleation Layer on Ferroelectricity of Hf_xZr_{1-x}O₂ Thin Films for Ferroelectric Field Effect Transistor Application

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Abstract

We demonstrated the superior ferroelectricity ($2P_r = 23 \mu\text{C}/\text{cm}^2$) in the TiN/Hf_xZr_{1-x}O₂/ZrO₂/TiN capacitor using the top-ZrO₂ nucleation layer. This is because the larger ferroelectric orthorhombic phase ratio was achieved by epitaxial like growth according to crystal direction of the top-ZrO₂ nucleation layer. Moreover, the leakage current density (J) can be reduced to 1/4 of the TiN/Hf_xZr_{1-x}O₂/TiN capacitor. Therefore, since the top-ZrO₂ nucleation layer technique can obtain the large $2P_r$ and low J , it is one of the effective methods for ferroelectric field effect transistors.

1. Introduction

Recently, Hf_xZr_{1-x}O₂ (HZO) thin films have been widely investigated for low power device applications such as ferroelectric FET (FeFET), due to its stable ferroelectricity even in extremely thin region (~10 nm) and CMOS applicability [1]. TiN electrodes are typically used as stressor layers to fabricate metal-ferroelectric-metal (MFM) capacitors with the HZO films because TiN electrodes provide the mechanical stress required for the formation of the unstable ferroelectric orthorhombic phase (o-phase) [2]. However, this method cannot be applied to FET structures. In our previous research, the HZO film crystallized using top- and bottom-ZrO₂ nucleation layers resulted in the large remanent polarization ($2P_r = P_r^+ - P_r^-$) [3].

In this study, we discuss the usefulness of the top-ZrO₂ nucleation layer technique on the ferroelectricity of the HZO film.

2. Experimental

Fig. 1 shows the schematic illustrations of (a) TiN/HZO/TiN (w/o) and (b) TiN/HZO/ZrO₂/TiN (T-ZrO₂) MFM capacitors. The T-ZrO₂ capacitor was fabricated as follows: First, TiN film as bottom electrode (BE-TiN) was deposited on SiO₂/Si substrate. A HZO film was subsequently deposited on the BE-TiN by atomic layer deposition (ALD) at 300°C using (Hf/Zr)[N(C₂H₅)CH₃]₄ (Hf/Zr = 1/1) cocktail precursor and H₂O gas. The thickness of the HZO film was varied from 10 to 25 nm. Next, a 2-nm-thick top-ZrO₂ layer was deposited on the HZO film by ALD at 300°C using (C₅H₅)₂Zr[N(CH₃)₂]₃ precursor and H₂O gas. After that, post-deposition-annealing (PDA) was carried out at 400-700°C for 1 min in a N₂ atmosphere. Finally, top TiN electrode (TE-TiN) was fabricated by DC sputtering. The TiN/HZO/TiN (w/o) capacitor was also prepared using the same process conditions. PDA was performed at same temperature condition after HZO film deposition.

3. Results and discussion

Fig. 1 shows the cross-sectional TEM images of (a) TiN/HZO (10 nm) and (b) TiN/HZO (10 nm)/ZrO₂ (2 nm) stacks after PDA treatment at 600°C. The HZO films in both stacks were crystallized. For the TiN/HZO/ZrO₂ case, vertical grain growth of the HZO film was observed from the polycrystalline top-ZrO₂ layer, while the HZO film of the TiN/HZO consists of many separate grains with sizes of 5-10 nm.

Fig. 2 shows the $2P_r$ of the w/o and T-ZrO₂ capacitors as a function of the HZO thickness. The inset graphs show P - E characteristics of the w/o and T-ZrO₂ capacitors with a 10-nm-thick HZO film. The T-ZrO₂ exhibited the superior $2P_r$ (23 $\mu\text{C}/\text{cm}^2$) compared to that (12 $\mu\text{C}/\text{cm}^2$) of the w/o. We found that the T-ZrO₂ maintains the larger $2P_r$ in all HZO thickness region. However, these $2P_r$ gradually degraded with increasing the HZO thickness.

Fig. 3 shows the $2P_r$ as a function of the PDA temperature. The w/o (PDA 700°C) exhibited a large leakage current (J) property. Noted that the $2P_r$ of the T-ZrO₂ were larger than those of the w/o under all PDA temperature conditions. The maximum $2P_r$ of both capacitors were obtained at the PDA 600°C. In addition, the T-ZrO₂ exhibited the high $2P_r$ (15 $\mu\text{C}/\text{cm}^2$) even in low temperature of 400°C, which was larger than the maximum $2P_r$ (12 $\mu\text{C}/\text{cm}^2$) of the w/o. Therefore, the top-ZrO₂ nucleation layer technique is one of the superior method due to its high $2P_r$ in wider PDA temperature ranges. To clarify these different $2P_r$ properties between the w/o and T-ZrO₂ capacitors, the crystal structures of the HZO films were evaluated by XRD analysis.

Fig. 4 shows the XRD patterns of the w/o and T-ZrO₂ capacitors with several HZO thicknesses. The diffraction peaks from the ferroelectric o-phase and the paraelectric monoclinic phase (m-phase) were clearly observed. Here, the relative ratio of o-phase was estimated from the peak area of o(111)/{m(-111)+o(111)+m(111)}. The relative ratio of o-phase as a function of the HZO thickness in the w/o and T-ZrO₂ summarizes in Fig. 5. ALD-ZrO₂ film consisted mainly of the o-phase or the tetragonal phase (not shown) [4]. Here, the epitaxial like growth of the HZO film must be started according to the crystal direction of the ZrO₂ nucleation layer. As a result, higher relative ratio of o-phase in the T-ZrO₂ could be obtained and results in the higher $2P_r$. On the other hand, the lower relative ratio of the o-phase in the w/o exhibited the lower $2P_r$. In addition, the relative ratio of o-phase of both capacitors decreases gradually as the HZO thickness increases. The dependence of the HZO

thickness on $2P_r$ (Fig. 2) can be understood easily according to this tendency. As shown in Fig. 5, the larger $2P_r$ and the lower J were achieved using the top-ZrO₂ nucleation layer. Based on these results, the top-ZrO₂ nucleation layer technique can be useful to design not only FeRAM but also FeFET applications.

4. Conclusions

We studied the effect of the top-ZrO₂ nucleation layer on the ferroelectricity and the crystalline of the HZO film. The $2P_r$ (23 $\mu\text{C}/\text{cm}^2$) of the T-ZrO₂ was almost 2 times larger than that (12 $\mu\text{C}/\text{cm}^2$) of the w/o. This is because the top-ZrO₂ layer plays an important role as the nucleation layer of the ferroelectric o-phase formation of the HZO film. In addition, the J value

of the T-ZrO₂ was lower than that of the w/o. These suggests that a HZO film with superior ferroelectricity can be obtained using the top-ZrO₂ nucleation layer technique even in the FeFET structure.

Acknowledgements

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References

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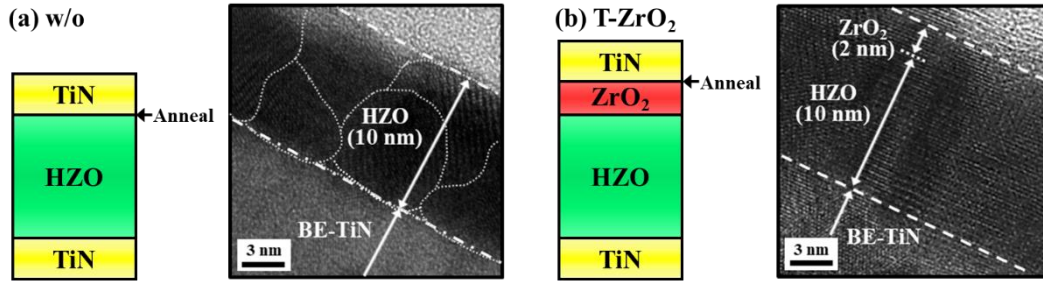


Fig. 1 Schematic illustrations and cross-sectional TEM images of PDA-treated (a) w/o and (b) T-ZrO₂ MFM capacitors with a 10-nm-thick HZO film. For the T-ZrO₂ case, epitaxial like growth of the HZO film started according to the top-ZrO₂ nucleation layer, while the HZO film of the w/o consists of many separate grains with sizes of 5-10 nm.

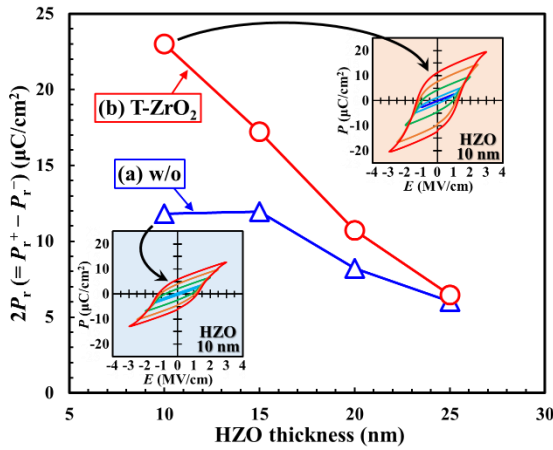


Fig. 2 $2P_r$ of the w/o and T-ZrO₂ capacitors as a function of the HZO thickness from P - E hysteresis curves. The maximum $2P_r$ (23 $\mu\text{C}/\text{cm}^2$) of the T-ZrO₂ with a 10-nm-thick HZO film was approximately 2 times larger than that (12 $\mu\text{C}/\text{cm}^2$) of the w/o.

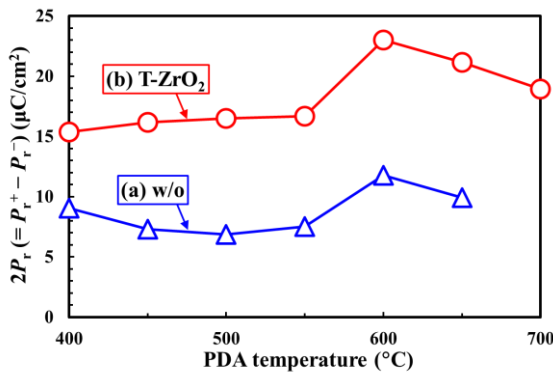


Fig. 3 $2P_r$ as a function of the PDA temperature from P - E field hysteresis curves. The $2P_r$ of the T-ZrO₂ were larger than those of w/o under all PDA temperature conditions.

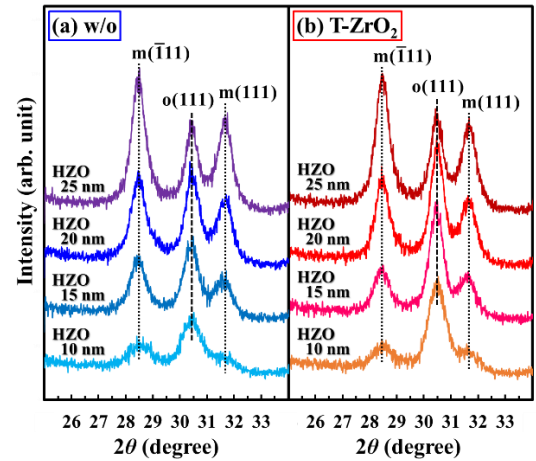


Fig. 4 XRD patterns of the w/o and T-ZrO₂ with several HZO thicknesses. The diffraction peaks from the ferroelectric o-phase and the paraelectric m-phase were clearly observed regardless of the HZO thickness.

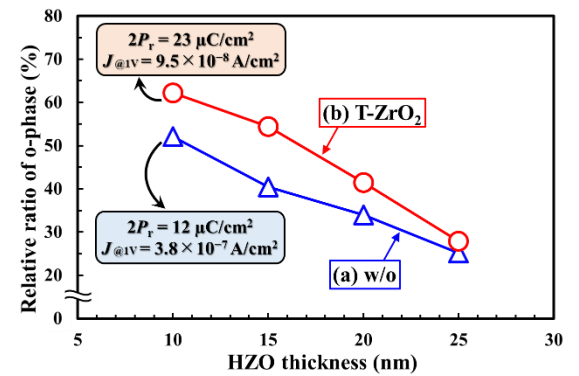


Fig. 5 Relative ratio of o-phase of the w/o and T-ZrO₂ as a function of the HZO thickness from XRD patterns. The T-ZrO₂ with a 10-nm-thick HZO film exhibited the maximum relative ratio of o-phase (62%), which was larger than that (52%) of the w/o.